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*Published in:*
Applied Physics Letters

*DOI:*
10.1063/1.3587630



*Publication date:*
2011

# Origin of the efficiency enhancement in ferroelectric functionalized organic solar cells

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(Received 25 March 2011; accepted 16 April 2011; published online 3 May 2011)

We have investigated the efficiency enhancement of organic solar cells upon incorporation of a thin ferroelectric polymer layer. For non-Ohmic contacts the enhancement is due to an increased open circuit voltage, which is, however, independent of the ferroelectric polarization direction. Ferroelectricity cannot play a role due to depolarization and charge compensation. The same improvement is also obtained with a non-ferroelectric fluorinated polymer. The data unambiguously show that the improved efficiency is solely due to improvement of the cathode. The fluorinated polymer layer plays the role of LiF in an optimized solar cell. © *2011 American Institute of Physics*. [doi:10.1063/1.3587630]

Organic solar cells are being considered as a promising candidate for low-cost power generation due to the possibility of roll-to-roll production.[1] Bulk heterojunctions of acceptor-donor blends have been proven a successful route toward efficient solution processable solar cells with power conversion efficiencies above 7%.[2] The research toward realization of higher efficiency bulk heterojunction solar cells is focused on two directions, viz., improvement in molecular design and synthesis of new polymers[3] and in improved solar cell device design. A prime example of the latter is tandem solar cells.[4]

In a recent article, Yuan *et al.*[5] reported on the efficiency enhancement in organic solar cells by incorporating a ferroelectric polymer interlayer between the electrodes and the photoactive layer. The enhanced efficiency was explained by the presence of an electric field due to the polarization of the ferroelectric layer, leading to enhanced exciton dissociation and, therefore, increased power conversion efficiency from 1%–2% to 4%–5%.[5] This additional electric field within the active layer of the solar cell has been claimed to be large, permanent, and eliminating the need for an external bias. However, to stabilize a ferroelectric polarization, compensation charges of both polarities are required on either side of the ferroelectric film. Without these compensating charges the ferroelectric cannot be permanently polarized due to the presence of a large depolarization field. In a pioneering work, Wurfel *et al.*[6–9] sandwiched a triglycine sulfate ferroelectric film between a metal electrode and a *p*-type silicon counter electrode. They experimentally demonstrated the existence of a depolarization field, which drastically reduces the ferroelectric polarization. In the case that the semiconductor is strongly illuminated, the photogenerated charge carriers provide the necessary compensation charges in the semiconductor, enabling poling of the ferroelectric. After switching off the light only half of the polarization loop was observed, since only accumulation of majority carriers can provide sufficient compensation.

Organic semiconductors are generally unintentionally doped semiconductors that lack the free carriers that are needed for stabilization of the ferroelectric polarization. For organic semiconductors in contact with the ferroelectric random copolymer poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] Naber *et al.*[10] have shown that polarization in metal-ferroelectric insulator-semiconductor diodes only occurs when majority carriers, in this case injected from a back contact, provide compensation. However, when the majority carriers are depleted, the ferroelectric depolarizes. In a recent study, we fabricated bistable switches using a phase separated blend film of P(VDF-TrFE) with the organic semiconductor regioirregular poly(3-hexylthiophene) (P3HT).[11] The ferroelectric polarization modulates the injection barrier of the semiconductor. To study the effect of depolarization an additional semiconductor layer was inserted in between the ferroelectric blend and the metal contact.[12] It was demonstrated that a semiconducting layer of only 50 nm completely suppresses permanent poling of the ferroelectric. The depolarization was confirmed by capacitance-voltage and retention time measurements. We note that the proposed structure of the ferroelectric functionalized solar cells has an identical layout, namely, a thin ferroelectric film with, in this case, a 150 nm thick semiconducting film on top. In the dark, the presence of a 150 nm thick undoped semiconductor will totally suppress the polarization of the ferroelectric due to the lack of free charge carriers that are needed to compensate the ferroelectric polarization. Poling of the ferroelectric in the dark will therefore not have any effect. An enhanced electric field due to ferroelectric polarization will not be present. Under illumination, however, the photogenerated charges will compensate the ferroelectric polarization charges and therefore will allow the ferroelectric to polarize. But since the photogenerated charge carriers screen the polarization also in this case there will be no enhanced electric field within the photoactive layer.

In order to address this controversial issue on the effect of ferroelectric layers on the power conversion efficiency of solar cells, we fabricated bulk heterojunction solar cells, similar to those reported recently. The efficiency of the ferro-

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electric functionalized cells when subjected to high voltage pulses for a prolonged time, increases irrespective of the polarity of the applied pulse. The efficiency approaches that of conventional cells fabricated with standard lithium fluoride (LiF) as an interlayer between the active layer and the cathode. This demonstrates that the improvement in the efficiency of the solar cell is due to improvement of the effective work function of the cathode and that the efficiency of the ferroelectric functionalized cells ultimately approaches to that of a device with an optimized cathode with LiF. The origin of the efficiency enhancement is confirmed by showing that the improved efficiency can also be achieved with fluorinated but non-ferroelectric polymers.

All solar cells used in this study were prepared using ITO coated glass substrates with resistivities of about 15 Ω/square. To supplement the ITO bottom electrode, a hole transport layer of PEDOT:PSS (Clevios P VPAI 4083) was spin-coated from an aqueous dispersion solution under ambient conditions, followed by drying the substrates at 140 °C for 10 min. Next, composite layers of regioregular poly(3-hexylethiophene) (P3HT; Rieke Metals) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM; Solenne) P3HT:PCBM (1:0.8 by weight) were spin-coated on top of the PEDOT:PSS layer. P3HT:PCBM solutions were prepared using chloroform as a solvent with a solid content of 15:12 mg/mL. The resulting film thickness amounted to 150 nm. The blends were annealed in a nitrogen atmosphere at 140 °C for 15 min. The random copolymer poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] and the polymer polytrifluoroethylene (PTrFE) were used as ferroelectric and nonferroelectric material, respectively. Both P(VDF-TrFE) (80-20) and PTrFE (Solvay Duphar, Belgium) were dissolved in acetone with a concentration of 2 mg/ml and spin-coated onto the blend film at 6000 rpm. We note that acetone is an orthogonal solvent for the P3HT:PCBM blend. The final film thicknesses of P(VDF-TrFE) and PTrFE were less than 5 nm as probed with atomic force microscopy. The films, however, showed many pinholes and were not homogeneous. Subsequently, all devices were annealed at 90 °C for 10 min to render P(VDF-TrFE) ferroelectric.[13] To complete the solar cells, Al electrodes, 100 nm, were deposited by thermal evaporation under vacuum ($1\times10^{-6}$ mbar). For the reference solar cell LiF (1 nm) and Al (100 nm) were directly deposited onto the blend. Device layout and the chemical structure of the compounds are given in Fig. 1(a). Current versus voltage characteristics were recorded using a Keithley 2400 SourceMeter. All preparation processes and electrical measurements were conducted in a $N_2$ atmosphere ($<1$ ppm $O_2$ and $<1$ ppm $H_2O$). To pulse the solar cells, a constant voltage of $\pm10$ V was applied in the dark on the P(VDF-TrFE)/Al and PTrFE/Al cathode, followed by a short-circuiting of 10 s. Illumination was carried out by means of a Steuernagel SolarConstant 1200, calibrated for spectral mismatch of the P3HT:PCBM cell spectral response with the solar spectrum. We note that our purpose in this manuscript is just examination of the origin of enhanced cell performance; hence optimization of the device performance is beyond the scope of our manuscript.

Figure 1(b) shows both the *J-V* characteristics of a reference cell with a standard LiF/Al cathode and the characteristics of a functionalized cell with a P(VDF-TrFE)/Al cathode. For the P(VDF-TrFE)/Al cell, the *J-V* curves were

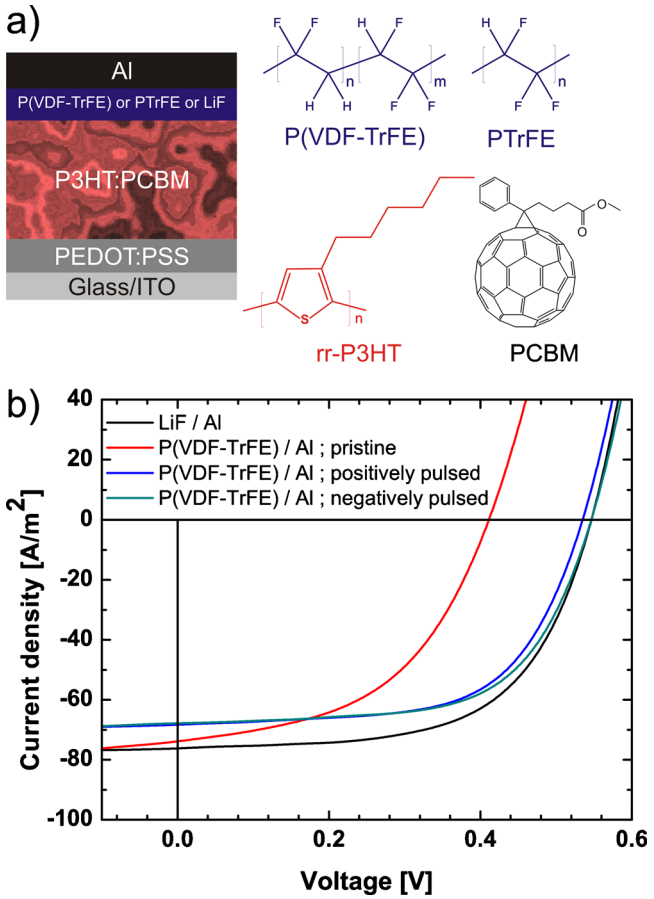


FIG. 1. (Color online) (a) Layout of the solar cells and chemical structure of the compounds used. (b) Comparison of the *J-V* characteristics under illumination of cells with P3HT:PCBM blend with different cathode configuration; LiF/Al (reference cell) and with a P(VDF-TrFE)/Al under different pulsing conditions.

measured as fabricated (pristine) and after subjecting the cell to either a positive voltage pulse of +10 V or a negative voltage of −10 V for 3 min to "polarize" the ferroelectric. The solar cell with a P(VDF-TrFE)/Al cathode in the pristine condition, thus, prior to application of pulse, behaves as one would expect for a cell with a non-Ohmic contact: the $V_{oc}$ is lowered by more than 0.1 V from that of the reference cell with the standard LiF/Al cathode. The fill factor (FF) has decreased as well, which is due to the reduced effective electric field.[14] Upon application of a voltage pulse and "polarizing" the ferroelectric layer, an Ohmic contact to the PCBM lowest unoccupied molecular orbital is restored and we obtain a $V_{oc}$ and FF equal to that of the reference cell with a LiF/Al cathode. Interestingly, the improvement is irrespective of the polarization direction of the ferroelectric layer; suggesting the improvement is not due to the ferroelectric polarization. Additionally it is important to note that the characteristics of the devices obtained in this way do not exceed those of the reference device.

To investigate the origin of the improved performance, dark current densities obtained in the P(VDF-TrFE)/Al cell were compared for different pulsing conditions. Figure 2 shows a comparison between the current densities of a pristine unpulsed solar cell and the same cell after being subjected to voltage pulses of +10 V and −10 V, respectively. What can be seen is that the current injection into the blend layer is improved, irrespective of the polarity of the applied

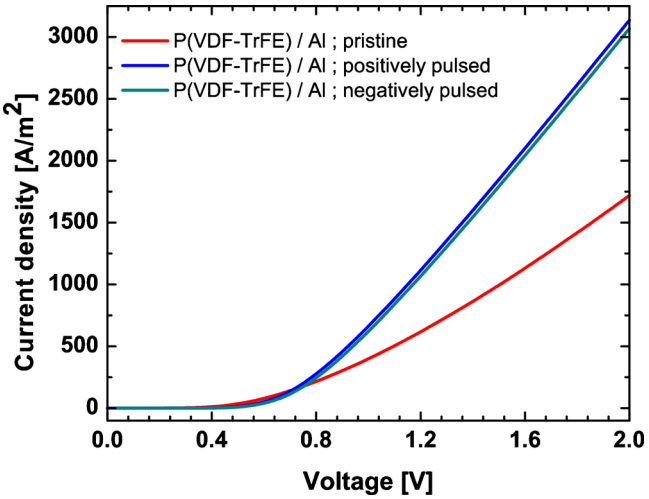


FIG. 2. (Color online) Comparison of the *J-V* characteristics of cells with a P3HT:PCBM blend with a P(VDF-TrFE)/Al cathode configuration in dark for the pristine unpulsed, positively pulsed, and negatively pulsed states.

voltage. These measurements suggest that ferroelectricity does not play a role in the improvement of the power conversion efficiency of the solar cell. One can therefore argue that prolonged application of a large voltage pulse only improves the electron injection and the extraction of the P(VDF-TrFE)/Al cathode.

To investigate this assumption, solar cells were prepared with a PTrFE/Al cathode instead of a P(VDF-TrFE)/Al cathode. As noted previously, PTrFE is semicrystalline with a chemical structure similar to P(VDF-TrFE), but it is non-ferroelectric.[15] The *J-V* characteristics of solar cells with a PTrFE/Al cathode are presented in Fig. 3. After applying voltage pulses of +10 and −10 V for 3 min, the cell's performance improves similarly compared to that of the unpulsed cell. Furthermore, we obtain the same increase in $V_{oc}$

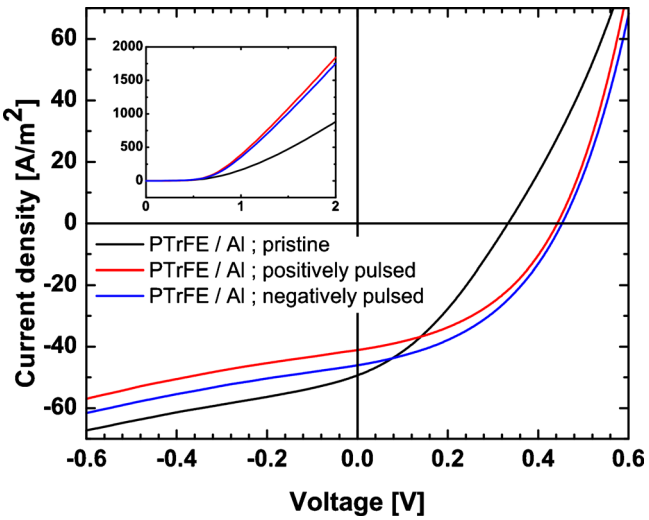


FIG. 3. (Color online) Comparison of the *J-V* characteristics of cells with a P3HT:PCBM blend with a PTrFE/Al cathode configuration in dark and under illumination for the pristine unpulsed, positively pulsed and negatively pulsed states. The inset shows the dark current densities of the device under the same pulsing conditions.

and FF for either pulse polarity. Moreover, we observe a same effect in the dark current of the devices similar to the cells with a P(VDF-TrFE)/Al cathode, as shown in the inset of Fig. 3. The increase in $V_{oc}$ is definitely not due to ferroelectricity. This result unambiguously leads us to the conclusion that the improved performance is caused by contact effects at the Al cathode and not by the creation of an internal field into the solar cell due to "ferroelectricity." The origin could very well be the electrochemical reaction between Al and PTrFE, or P(VDF-TrFE) due to prolonged application of a high voltage.

Using only Al as a cathode in a solar cell leads to a suboptimal device design. Since the work function of Al is too high, the built-in electric field and the $V_{oc}$ of the solar cell will be limited. In standard devices, this is solved by adding a thin LiF layer that lowers the work function.[14] In the P(VDF-TrFE) and PTrFE functionalized solar cells the same is done by adding a fluorinated polymer layer. As a result the novelty of this "ferroelectric" approach is to replace LiF by P(VDF-TrFE) or PTrFE.

In summary, we have argued that ferroelectric functionalized organic solar cells, with a "truly" ferroelectric interlayer will be subjected to ferroelectric depolarization. We have demonstrated that inserting a layer of a ferroelectric polymer in the solar cell stack only leads to improved power conversion efficiency for non-optimized solar cells with non-Ohmic contacts. In the best-case scenario, the performance of the "ferroelectric-material" functionalized solar cell approaches that of optimized cells with standard LiF/Al cathodes.

We would like to acknowledge Jan Harkema and Mengyuan Li for technical assistance, and financial support by Zernike Institute for Advanced Materials, the EC project under FP7 Contract No. 212311, ONE-P and the Dutch Polymer Institute (DPI) under Project DPI No. 660.

[1]P. W. M. Blom, V. D. Mihailetchi, L. J. A. Koster, and D. E. Markov, Adv. Mater. **19**, 1551 (2007).
[2]Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, and L. Yu, Adv. Mater. **22**, E135 (2010).
[3]A. W. Hains, Z. Liang, M. A. Woodhouse, and B. A. Gregg, Chem. Rev. **110**, 6689 (2010).
[4]A. Hadipour, B. de Boer, and P. W. M. Blom, Adv. Funct. Mater. **18**, 169 (2008).
[5]Y. Yuan, T. J. Reece, P. Sharma, S. Poddar, S. Ducharme, A. Gruverman, Y. Yang, and J. Huang, Nature Mater. **10**, 296 (2011).
[6]P. Wurfel, I. P. Batra, and J. T. Jacobd, Phys. Rev. Lett. **30**, 1218 (1973).
[7]P. Wurfel and I. P. Batra, Phys. Rev. B **8**, 5126 (1973).
[8]I. P. Batra, P. Wurfel, and B. D. Silverman, Phys. Rev. B **8**, 3257 (1973).
[9]I. P. Batra and B. D. Silverman, Solid State Commun. **11**, 291 (1972).
[10]R. C. G. Naber, J. Massolt, M. Spijkman, K. Asadi, P. W. M. Blom, and D. M. de Leeuw, Appl. Phys. Lett. **90**, 113509 (2007).
[11]K. Asadi, D. M. de Leeuw, B. de Boer, and P. W. M. Blom, Nature Mater. **7**, 547 (2008).
[12]K. Asadi, J. Wildeman, P. W. M. Blom, and D. M. de Leeuw, IEEE Trans. Electron Devices **57**, 3466 (2010).
[13]R. G. Kepler and R. A. Anderson, Adv. Phys. **41**, 1 (1992).
[14]V. D. Mihailetchi, L. J. A. Koster, and P. W. M. Blom, Appl. Phys. Lett. **85**, 970 (2004).
[15]H. S. Nalwa, *Ferroelectric Polymers* (Marcel Dekker, Inc., New York, 1995).